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Hydroxyapatite With Environmental Applications

C.L. Popa[a,b], C.S. Ciobanu[a], C.C. Petre[c], M. Motelica-Heino[d], S.L. Iconaru[a,b,d], G. Jiga[c], D. Predoi[a*]

[a]*National Institute of Materials Physics , P.O. Box MG 07, Bucharest, Magurele, Romania*

[*]*dpredoi@gmail.com*

[b]*Faculty of Physics, University of Bucharest, 405 Atomistilor, CP MG-1, 077125 Magurele, Romania*

[c]*University Politehnica of Bucharest, Faculty of Engineering and Management of Technological Systems, Department of Strength of Materials,060032, Bucharest, Romania*

[d]*ISTO, UMR 7327 CNRS-Université d'Orléans, 1A rue de la Férollerie 45071 Orléans Cedex 2, France*

Abstract. The aim of this study was to synthetize new nanoparticles based on methyltrimethoxysilane coated hydroxyapatite (MTHAp) for lead removal in aqueous solutions. The morphological and compositional analysis of MTHAp was investigated by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). Removal experiments of Pb^{2+} ions were carried out in aqueous solutions with controlled concentration of Pb^{2+} and at fixed pH of 5. After the removal experiment of Pb^{2+} ions from solutions, porous hydroxyapatite nanoparticles were transformed into PbMTHAp_5 via the adsorption of Pb^{2+} ions followed by a cation exchange reaction. Our results demonstrate that the porous hydroxyapatite nanoparticles can be used as an adsorbent for removing Pb^{2+} ions from aqueous solution.

Keywords: methyltrimethoxysilane, hydroxyapatite, lead removal

INTRODUCTION

One of the major environmental problems is represented by the global contamination with potentially toxic trace elements (PTTE). Lead has been widely used in the industrial field, for lead-based batteries, ammunition, paints and building materials [1-4]. Due to their non-biodegradable behaviour and their incapacity of metabolization and decomposition, PTTE like Pb, Cu, Cd, Zn and Hg are the main contaminants of soils and ground or surface waters. Their progressive accumulation in the human body can cause significant health problems, inducing chronic illness which untreated, can lead to a painful death.

Among a large variety of PTTE, one of the most dangerous is lead. Recently, the International Agency for Research on Cancer (IARC) has included lead in the list of possible human carcinogens (IARC, 1987) together with its inorganic compounds (IACR 2006) [5]. Therefore, researchers world-wide have focused on developing new and improved methods for removing PTTE from the different environmental compartments such as soils and waters.

In the last decades, a major attention has been given to a special material, hydroxyapatite (HAp) $[Ca_{10}(PO_4)_6(OH)_2]$ due to its remarkable properties. On the other hand, hydroxyapatite (HAp) has a high sorption capacity for actinides and divalent metals [6-7]. Furthermore, previous studies have revealed a high capacity for removing divalent ions from aqueous solutions [8-16] and contaminated soils [6-17]. For the removal of PTTE from polluted media by synthetic HAp different mechanisms have been reported, like ion exchange [18-21] and substitution of Ca ions in HAp by metals ions [6, 18, 22]. In order to improve the capacity of adsorption, it was shown that there are several factors that must be take into account, among them the type of divalent metal, the physico-chemical properties of HAp, the metal concentration, the solution pH, etc. [23-25].

The aim of this study was thus to prepare methyltrimethoxysilane coated hydroxyapatite (MTHAp) composite powders at nanoscale and to investigate Pb^{2+} ions removal from aqueous solutions using MTHAp samples. The morphological and compositional analysis of MTHAp was investigated by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). Batch experiments at a fixed pH of 5 were conducted with the powders and solutions of lead.

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Results and Discussions

Methyltrimethoxysilane coated hydroxyapatite (MTHAp) was prepared using methyltrimethoxysilane and hydroxyapatite. The hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) nanoparticles were prepared by setting the atomic ratio of Ca/P at 1.67 in accord with [26]. The hydroxyapatite (HAp) was immobilized into a methyltrimethoxysilane foam using the technique reported in the literature [27]. MTHAp was obtained when methyltrimethoxysilane solution (1 g HAp/10 ml) was dropped on the HAp powder. The mixtures were then stirred vigorously for 30 min until homogeneity was achieved. After forming stable structures, MTHAp composites were allowed to dry in a vacuum oven at 80°C for 24 h for the the excess solvent to evaporate. Finally, MTHAp composite samples were then ground to obtain powders.

Removal performance of Pb^{2+} ions by the MTHAp composite powders was investigated by batch experiments and monitoring the change of Pb^{2+} ion concentration in the aqueous solution. For these experiments, 5 g of MTHAp composite sample was put into 500 ml aqueous solution with various initial Pb^{2+} ion concentrations and pH values in accord with Suk Hyun Jang et al. [8]. The initial Pb^{2+} ion concentrations of the aqueous solutions were controlled and the values were set in the range 0.1-0.9 $g{\cdot}L^{-1}$ by dissolving lead nitrate [$Pb(NO_3)_2$] in deionized water. The pH value of aqueous solutions with a controlled initial Pb^{2+} ion concentration was adjusted to 5 by adding small amounts of 0.1M HCl standard solution. For all experiments the solution was stirred constantly for 24 h by a mechanical stirrer at room temperature.

Scanning electron microscopy (SEM) study was performed on a HITACHI S2600N-type microscope equipped with an energy dispersive X-ray attachment (EDAX/2001 device).

The hydroxyapatite coated with methyltrimethoxysilane before and after the reaction with the Pb^{2+} ion-containing solution with pH 5 for 24 h were investigated by SEM and results are presented in Figure 1. Distinct morphologies were observed in the SEM micrographs. The presence of $Pb_{10}(PO_4)_6(OH)_2$ crystals were identified by crystal clusters with needle or rod-like shapes. These results are in good agreement with preliminary studies performed by Cheol Y. Kim et al. [28].

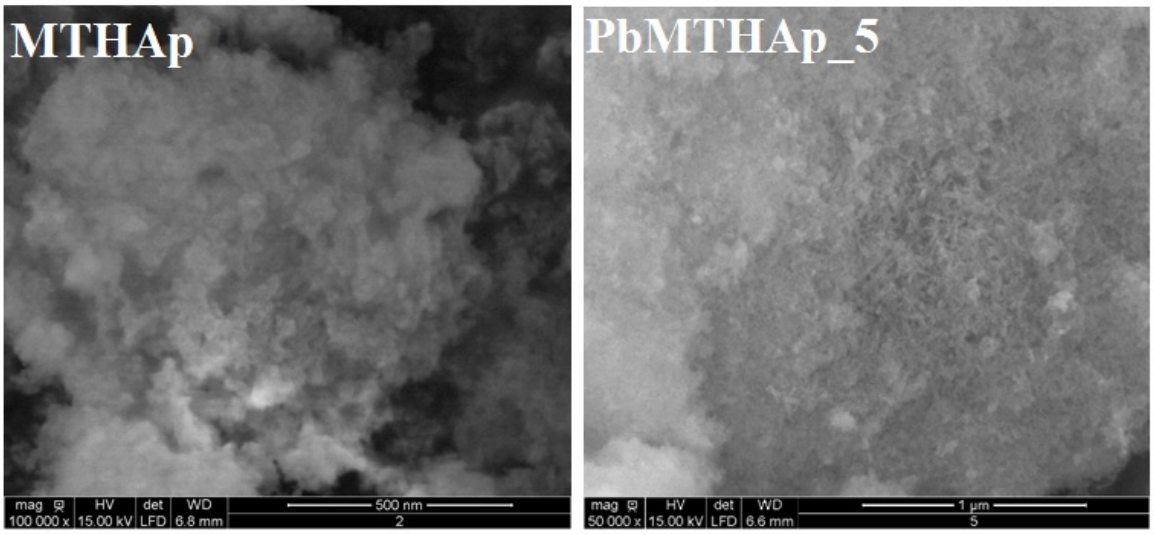

Figure 1: SEM micrographs of hydroxyapatite coated with methyltrimethoxysilane (MTHAp) before and after the reaction with a solution containing 950 mg of Pb/L at pH 5 (PbMTHAp_5).

The concentration of Pb^{2+} ions remaining in the solution after the MTHAp reacted with the Pb^{2+} ion-containing solution was determined by flame atomic absorption spectroscopy (Hitachi Z-8100 spectrophotometer).

The impact of the concentration of lead in the aqueous solution was studied by absorption experiments realized at 25°C within MTHAp and with a concentration range of 0.1– 0.9 $g{\cdot}L^{-1}$ at pH 5. Measurements were performed on 500 mL solution (pH 5) with an initial Pb^{2+} ion concentration of 63 $mg{\cdot}L^{-1}$. Figure 2 presents the adsorption efficiency of Pb^{2+} ions as a function of the Pb concentration in solution. It was noticed that the removal efficiency increased proportional with the Pb concentration. When a Pb concentration of 0.1 $g{\cdot}L^{-1}$ was used, the

removal efficiency reached 98.4%, showing that the adsorbent composite, MTHAp, had a strong affinity to the Pb^{2+} ions. At Pb concentration from 0.5 $g \cdot L^{-1}$ to 1.5 $g \cdot L^{-1}$, the removal efficiency was nearly 100%. In this case, the Pb^{2+} ions in the solution were completely removed. For the studies on the effect of the solution pH, the lead concentration dosage of 0.9 $g \cdot L^{-1}$ was selected.

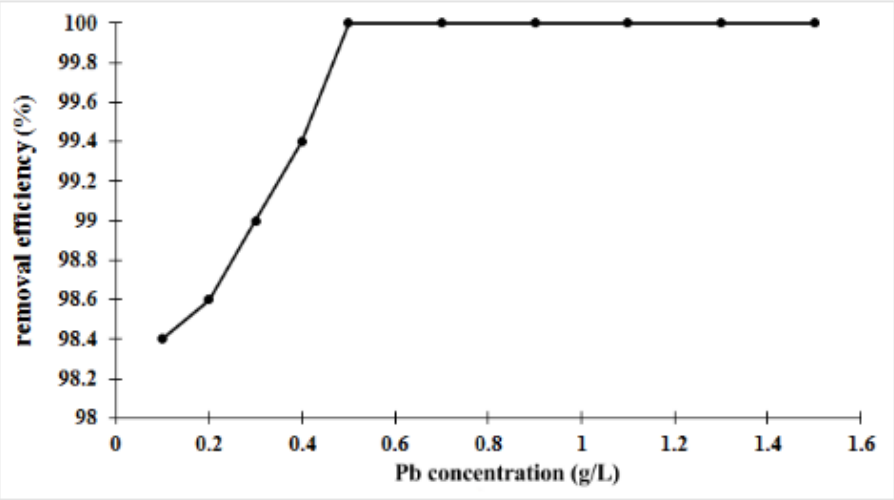

Figure 2: Effect of the Pb concentration on the removal of the Pb^{2+} ions by MTHAp.

Following these results, it can be emphasized that MTHAp can effectively remove Pb^{2+} ions from the aqueous solution. In agreement with previous studies [3], the formation of the new crystals was identified. Distinct morphologies were observed in the SEM micrographs. Scattered needle- or rod-shaped crystals were observed in the sample obtained from the reaction performed at pH 5. Q. Y. Ma et al. [29] reported similar crystals in previous studies. This research showed that the MTHAp nano-composite material is a promising adsorbent for Pb^{2+} ions from aqueous solution at various pH values and could be used as a wastewaters purifier.

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